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TECHNICAL REPORT ARCCB-TR-88033

DETERMINATION OF ETHYLENE GLYCOL DEGRADATION PRODUCTS IN CHROMIUM PLATING AND ASSOCIATED POLISHING SOLUTIONS BY ION CHROMATOGRAPHY

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AUGUST 1988

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCCB-TR-88033	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DETERMINATION OF ETHYLENE GLYCOL DEGRADATION PRODUCTS IN CHROMIUM PLATING AND ASSOCIATED POLISHING SOLUTIONS BY ION CHROMATOGRAPHY		5. TYPE OF REPORT & PERIOD COVERED Final 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Samuel Sopok		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS US Army ARDEC Benet Laboratories, SMCAR-CCB-TL Watervliet, NY 12189-4050		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS AMCMS No. 6126.23.1BL0.0 PRON No. 1A72ZJ7BNMSC
11. CONTROLLING OFFICE NAME AND ADDRESS US Army ARDEC Close Combat Armaments Center Picatinny Arsenal, NJ 07806-5000		12. REPORT DATE August 1988 13. NUMBER OF PAGES 5
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted to LC-GC Magazine of Liquid and Gas Chromatography.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Ethylene Glycol
Acid Degradation Products
Chromium Plating Solutions
Polishing Solutions
Ion Chromatography

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Ethylene glycol resulting from cooling system leaks can adversely affect plating properties when added to chromium plating and associated polishing solutions. Ion chromatography can be used to monitor these leaks by quantitatively determining the glycolic, oxalic, and formic acid degradation products of ethylene glycol.

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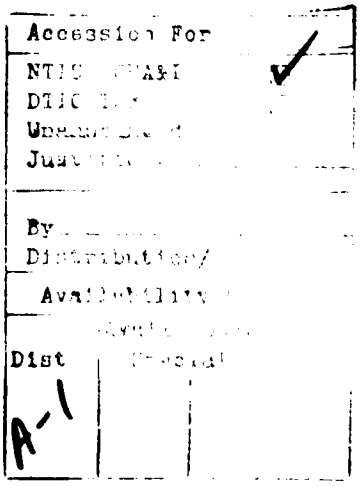
TABLE OF CONTENTS

TABLES



INTRODUCTION

Many general methods (refs 1,2) exist for determining organic acids by high performance ion chromatography exclusion (HPICE). Past investigations (refs 3,4) have shown that ion chromatography exclusion is useful for determining the organic acid degradation products of ethylene glycol used in solar energy collectors. The oxidative properties of both chromium plating and associated polishing solutions also produce organic acid degradation products of ethylene glycol which compromise plating quality (refs 5,6).

A method is given here using HPICE for monitoring and determining organic acid degradation products due to ethylene glycol coolant leaks in chromium plating and associated polishing solutions.

EXPERIMENTAL PROCEDURE

The analysis system is the Dionex model 2020i ion chromatograph and the Dionex model 4270 integrator (attenuation is 1024). The system flowstream consists of the eluent reservoir (0.001 M hydrochloric acid), eluent delivery system (1.0 mℓ/min), injector valve (100 μℓ), separator column (Dionex, HPICE-AG1), suppressor column (Dionex, ISC), and conductivity detector (Dionex, 10 μS).

Calibration standards are composed of only glycolic, oxalic, and formic acids since the presence of sulfuric, phosphoric, or chromic acids would decompose the organic acids.

Samples are composed of 25 mℓ of reagent grade ethylene glycol and 975 mℓ of either chromium plating or associated polishing solutions. The chromium plating solution contains 2.50 g/ℓ sulfuric acid and 250 g/ℓ chromic acid, while

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References are listed at the end of this report.

the polishing solution contains 680 g/ℓ phosphoric acid and 840 g/ℓ sulfuric acid. The sample solutions are each allowed to react with ethylene glycol for two hours under stirred conditions allowing gases to evolve. Although vigorous evolution of carbon dioxide subsides after ten minutes, these samples are stirred for two hours to assure that degradation products equilibrate in these metal finishing solutions. After stirring, each sample requires a 250 dilution before analysis.

RESULTS AND DISCUSSION

In Table I, the first three solutions provide calibration data for glycolic, oxalic, and formic acids which are organic acid degradation products of ethylene glycol in chromium plating and associated polishing solutions. Solutions four and five in Table I contain the respective results of chromium plating and associated polishing solutions for determinations of these organic acid products of ethylene glycol. For all solutions in Table I, the retention times of glycolic, oxalic, and formic acids are 11.7, 7.0, and 12.8 minutes, respectively.

TABLE I. DETERMINATION OF DEGRADATION PRODUCTS OF ETHYLENE GLYCOL

Solution	Glycolic Acid		Oxalic Acid		Formic Acid	
	Conc.(ppm)	H(μS)	Conc.(ppm)	H(μS)	Conc.(ppm)	H(μS)
1	10	2.61	10	4.09	10	3.53
2	20	5.19	20	8.19	20	7.00
3	30	7.71	30	11.93	30	10.50
4	2	0.40	12	4.85	15	5.41
5	4	1.11	19	7.62	26	9.10

As suggested elsewhere (refs 3-5), the oxidative degradation of ethylene glycol has ordered steps in these metal finishing solutions that include glycolic, oxalic, formic, and carbonic acids. In these chromium plating solutions, trivalent chromium is a by-product of the oxidation of ethylene glycol. The composition of ethylene glycol degradation products depends on acid composition, acid concentration, reaction time, and reaction temperature.

A contributing factor in the success of this method is that HPICE does not retain cations, sulfate, phosphate, or chromate, and no interference exists between these non-retained species and the retained organic acid analytes.

In addition to the analytes mentioned, there is a very small peak at 15.3 minutes with a height of 0.1 μS that appears to be carbonic acid, but this is difficult to investigate in acidic solutions and eluent. There is a great deal of carbonic acid liberated by the oxidation process and it is reasonable to assume that some is still present under weak acidic conditions.

This method provides a baseline resolution of analyte peaks and quantitatively determines these analytes to parts per million levels in these metal finishing solutions.

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